

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN AND RELATING TO POLYMERS

(71) We, ALLIED COLLOIDS LIMITED, a British Company, of Low Moor, Bradford, Yorkshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention concerns improvements in and relating to polymers. It relates particularly to a process for the production of water-soluble polymers, wherein the monomer is dispersed in a continuous oil phase during the polymerisation reaction.

The water-in-oil emulsion polymerisation of water-soluble monomers is well-known and has several advantages over other modes of polymerisation. Thus, for example the polymerising medium retains a low viscosity throughout the course of the reaction thereby obviating the difficulties of heat transfer associated with viscous polymerising solutions. The physical nature of the latex product also facilitates its handling and further processing. Another important advantage of emulsion polymerisation over mass or solution processes is that it allows the attainment of higher molecular weight products at faster reaction rates than is possible in the latter processes.

In order to stabilise such systems during emulsion polymerisation it is necessary to have present a suitable emulsifying agent. Those preferred for water-in-oil emulsions have a low hydrophilic lipophile balance as defined in the well known Atlas HLB classification. Typical examples of such surface active agents are sorbitan esters such as the monooleate and mono-stearate.

Commercially it is desirable to produce final dispersions with as high a polymer content as possible, and polymer concentrations in excess of 30% by weight of the total latex are particularly attractive. Addition polymerisation is an exothermic process and unless adequate steps are taken to remove heat from the polymerising system its temperature will rise appreciably, and alter the characteristics

of the polymerisation. With high concentrations of monomer this exotherm and the need to dissipate the heat of reaction can limit the rate at which the polymerisation can be carried out. Many of the water-soluble monomers of interest, such as acrylamide and acrylic acid and its salts and esters, have high intrinsic rates of polymerisation and it is essential to control the rate of the process in order to contain the temperature rise within practicable limits.

One method of achieving such control is the gradual addition of the monomer charge to the system while the polymerisation is proceeding. By adjusting the rate of addition so that it is in balance with the rate of polymerisation it is possible to limit the concentration of free monomer, and thus the rate of heat of evolution, throughout the reaction.

However, the addition of aqueous monomer to the reacting emulsion produces instability and can lead to coagulation of the product if only the conventional water-in-oil emulsifier is present. We have found that if the continuous oil phase contains certain copolymers in solution then this imparts sufficient stability to the reacting system to allow the continuous addition of the aqueous monomer charge during the polymerisation and the risk of coagulation is at least minimised. The presence of the stabilising copolymer enables one to prepare in one stage a dispersion containing a high concentration of polymer, for example of the order of 30–35% by weight of the total latex.

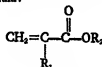
According to the present invention there is provided a process for the preparation of a stable dispersion of polymer by emulsion polymerisation which comprises continuously introducing an aqueous solution of monomer to a system containing oil, water-in-oil emulsifier, an emulsion stabilizer which is an oil-soluble copolymer prepared from at least one hydrophobic monomer and at least one hydrophilic monomer, and polymerisation initiator, the system being at the temperature required for polymerisation whereby to effect

the polymerisation throughout the continuous addition of monomer.

- 5 The polymer as preferably derived from water-soluble vinyl monomer. The emulsion "stabiliser" is suitably prepared from at least one hydrophobic monomer (Type A) and at least one hydrophilic monomer (Type B) in a molar ratio of Type A: Type B in the range 1:3 to 3:1. The copolymer need not be a binary copolymer.

- 10 Since the aqueous monomer is added over a period of time all references to the aqueous phase are to the total amount thereof.

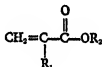
- 15 Typical type A monomers are represented by the formula:



- 20 where R_1 is H or CH_3 and R_2 can be $\text{C}_n\text{---C}_{25}$ hydrocarbon chain either branched or linear. Representative of Type A monomers are the fatty esters of methacrylic or acrylic acid containing twelve or more carbon atoms in the ester group. Examples of these are lauryl acrylate and steryl methacrylate.

- 25 Typical type B monomers which may be anionic, nonionic or cationic are represented by the following formulae:

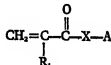
anionic



where

- 30 $\text{R}_1 = \text{H}$ or CH_3
 $\text{R}_2 = \text{H}$

nonionic



where

- 35 $\text{R}_1 = \text{H}$ or CH_3
 $\text{X} = \text{NH}$ or O
 $\text{A} = (\text{CH}_2\text{---CH}_2\text{O})_n\text{---H}$ where
 $n = 1$ to 20

cationic

- 40 $\text{CH}_2=\underset{\text{R}_1}{\text{C}}-\overset{\text{O}}{\underset{\text{X}}{\text{C}}}-(\text{CH}_2)_n-\text{N}^+\begin{matrix} \text{R}_2 \\ \text{R}_3 \end{matrix}$

where

$\text{R}_1 = \text{H}$ or CH_3

R_2 and R_3 are independently selected from

C_1 to C_4 hydrocarbon

$\text{X} = \text{O}$ or NH

$n = 1$ to 3

Representative of Type B monomers are the dialkylamino ethyl esters of acrylic or methacrylic acid, for example, diethylamino ethyl acrylate, dimethylaminoethyl methacrylate or di-tertiary butyl aminoethyl methacrylate. Also in this class are acrylic acid and methacrylic acid and their salts as well as acrylamide and methacrylamide. The type B monomer may also be a polyethoxylated vinyl compound.

The most preferred range for the molar ratio of Type A:Type B monomers lies in the range 1:2 to 2:1. The most effective ratio depends on the choice of monomers for the emulsion stabiliser, and also the monomer or monomers to be polymerised in the inverse emulsion system.

The emulsion stabilisers may be produced for example by solution polymerisation in a common solvent for the monomers which may be all present initially or can be added continuously during the polymerisation, which may be initiated by a conventional free radical initiator such as azo-bis-isobutyronitrile (AZDN) or benzoyl peroxide both of which decompose thermally; or by a reduction-oxidation initiation system e.g. hydroperoxide in conjunction with polyethylene polyamine to give initiation at lower temperature. As the emulsion stabiliser must be soluble in the oil phase used in the subsequent emulsion polymerisation, it is advantageous to carry out its preparation in this oil, but other solvents may be used when more convenient. The emulsion stabiliser imparts stability to the emulsion polymerisation system by virtue of its amphipathic characteristics such that the hydrophilic parts of the chain will tend to attach to the dispersed aqueous particles whilst the hydrophobic chains extend from the particle surface into the continuous phase. The levels used to impart sufficient stability to a continuous addition polymerisation preferably fall in the range 0.1-10 parts for each 100 parts by weight of aqueous monomer solution to be added. The amounts of conventional inverse emulsifier employed are preferably in the range 0.1 to 10 parts per 100 parts by weight aqueous monomer solution.

The range of water-soluble monomers which may be polymerised by the process of this invention is extensive and includes for example acrylamide, methacrylamide; acrylic acid or methacrylic acid and their water-soluble esters such as the quaternary ammonium salts or acid salts derived from diethylaminoethyl acrylate and from dimethylaminoethylmethacrylate; vinyl sulphonic acid and its salts--and the salts of N-vinylpyridine and homologues. Copolymers of such mono-

mers can also be produced by this technique. The concentration of monomer in the aqueous solution used as feedstock in this polymerisation can vary over a range from 20% to 90% by weight of the solution. The preferred solution concentration is 40% to 60% by weight. The disperse phase to total emulsion can vary over a range from 25% to 75%.

The oil phase can be any inert hydrophobic liquid which is immiscible with the disperse monomer-containing phase for example an aromatic hydrocarbon, such as toluene or xylene, or an aliphatic hydrocarbon including a range of petroleum fractions. Halogenated hydrocarbons with a low reactivity towards free radicals can also be employed and perchloroethylene is an example of such a hydrocarbon.

The monomers employed in this invention polymerise by a free radical mechanism and the reaction is initiated at elevated temperatures by the thermal decomposition of an initiator such as for example azo-bis-isobutyronitrile, azobiscyclohexanenitrile, benzoyl peroxide, lauroyl peroxide, potassium persulphate or other persulphate salt. The initiator may be soluble in either the continuous oil phase or in the disperse monomer/polymer phase. The level of initiator used lies in the range 0.005 to 0.5 per cent by weight of the final emulsion system. Temperatures in the range 50°C. to 90°C. give suitable reaction rates and products.

In one specific embodiment for carrying out the continuous emulsion polymerisation of the invention the oil medium, containing both the water-in-oil emulsifier and the emulsion stabiliser, is charged to the reaction vessel and has oxygen removed from it by sparging with pure nitrogen or by repeatedly reducing the pressure above it to a low level and repressurising with pure nitrogen. The oil is then brought to the desired temperature for the reaction and the free radical initiator added either directly as solid or in a suitable solvent in such a way to maintain an atmosphere of nitrogen above the mass. The aqueous monomer solution is then added to the reaction vessel continuously over a period of time such that there is never a large amount of free unpolymerised monomer present in the system at any time. The period of addition may range from 0.5 to 10 hours but is usually in the range 1 to 3 hours. In order to maintain a continuous polymerisation it is often essential to remove dissolved oxygen from the aqueous monomer solution before addition to the reaction vessel. This may be done by sparging with purified nitrogen. The aqueous monomer solution is added to the oil to give a final ratio of oil to aqueous phase in the range 3:1 to 1:3 the preferred ratio being approximately 1:2, all ratios being related to the final weights of the phases. The product

is a milk-white to buff coloured cream-like dispersion. The polymer may be isolated by pouring the dispersion into a suitable precipitating medium such as acetone, and filtering and drying the resultant precipitate.

More especially the dispersion in oil may be used directly by adding it to an excess of well-stirred water when the water-in-oil dispersion is destabilised and inverts to give an oil-in-water system. The polymer is thus dissolved in the water to give aqueous polymer solutions of a wide range of viscosities which are suitable for use in industrial processes for example as flocculants, thickeners, filtration aids de-watering agents for sludges or dispersants.

The invention is illustrated by the following Examples.

EXAMPLE I

(a) Preparation of dimethyl amino ethyl methacrylate: stearyl methacrylate stabilizer

The following monomeric mixture was charged into a 3 litre reaction vessel equipped with a stirrer, reflux condenser, nitrogen bubbler and thermometer: 100 parts by weight monomer (48.7 parts of dimethyl amino ethyl methacrylate and 51.3 parts of stearyl methacrylate); 76.7 parts light spindle oil some of which is used for dispersing both the initiator and the chain transfer agent. The vessel was heated up to 70°C, and the stirred mixture was nitrogen purged for 20 minutes. The bubbler was then raised above the liquid level and the chain transfer agent and the initiator were charged into the vessel [3.74 parts of azo - bis - isobutyronitrile and 1000 p.p.m. of 2 - mercapto ethanol (based upon the monomer weight)].

Thus the initial polymerisation was carried out at 55% solids and an exotherm in the range 18—23°C was observed. 90 minutes after the initiation a further 72.1 parts of nitrogen bubbled light spindle oil was added to the vessel which was then maintained at 90°C for 3 hours. After this time the stabilizer was diluted to 25% W/W solids with 148.7 parts of light spindle oil.

(b) Inverse emulsion polymerisation of methyl chloride quaternised dimethyl amino ethyl methacrylate

Into a 700 millilitre reaction vessel equipped with a stirrer, reflux condenser, nitrogen bubbler and thermometer was charged 55.5 parts by weight of light spindle oil, 3.64 parts sorbitan monolaurate, and 8 parts of the 25% stabilizer prepared as in (a) above. The vessel was heated up to 70°C and the stirred mixture was nitrogen purged for 20 minutes. The bubbler was then raised above the liquid level and the initiator was charged into the vessel [500 p.p.m. of azo - bis - isobutyronitrile (based upon monomer phase)].

100 parts of a 60% solution of methyl chloride quaternised dimethyl amino ethyl methacrylate was added slowly to the reaction vessel over a 2 hour period. After the monomer addition was complete the vessel was maintained at 70°C for a further 1½ hours to complete the polymerisation. A sample of the emulsion was precipitated in acetone, washed twice and then filtered and dried at 60°C for half an hour. The viscosity of a 1% solution from this reaction was 487 c.s. through a 3A suspended level viscometer.

EXAMPLE II

(a) Preparation of ditertiary butyl amino ethyl methacrylate: stearyl methacrylate stabilizer

214.8 parts of light spindle oil was charged into a 3 litre reaction vessel maintained at 75°C and equipped as in Example I, utilising the same purging procedure. This was then followed by the addition of 0.5 parts of azo-bis - iso - butyronitrile (A.Z.B.N.), 100 parts of monomer (consisting of 59.2 parts of ditertiary butyl amino ethyl methacrylate and 40.8 parts of stearyl methacrylate) was then added continuously to the reaction vessel over a 62 minute period. Half an hour after the addition was complete the temperature was increased from 75°C to 90—95°C. and was maintained at this temperature for 4½ hours. The final stabilizer concentration was 31.8% W/W solids.

(b) Inverse emulsion polymerisation of methyl chloride quaternised dimethyl amino ethyl methacrylate.

Into a 700 millilitre reaction vessel equipped as in Example I was charged 58.2 parts of light spindle oil, 3.64 parts of sorbitan mono-laurate, and 9.1 parts of the 31.8% stabilizer prepared as in (a) above. The same purging procedure as Example I was employed followed by the addition of 120 p.p.m. of A.Z.B.N. based upon the monomer phase. 100 parts of a 51.9% solution of methyl chloride quaternised dimethyl amino ethyl methacrylate was added continuously to the reaction vessel over a 126 minute period. After the monomer addition was complete the vessel was maintained at 70°C for a further 1 1/4 hours to complete the reaction. A 1% solution of the inverted emulsion in water yielded a viscosity of 5200 c.p.s. measured by a Brookfield Viscometer.

EXAMPLE III

(a) Preparation of acrylamide:stearyl methacrylate stabilizer

100 parts by weight of a monomer mixture, consisting of 17.35 parts of acrylamide and 82.65 parts of stearyl methacrylate was dissolved in 156 parts of tertiary butyl alcohol. This monomer mixture was added continuously over 1½ hours into a 3 litre reaction vessel

equipped as in Example I utilising the same purging procedure; containing 58 parts of t-butyl alcohol and 2 parts of A.Z.B.N. The reaction vessel was maintained at 75°C to 80°C throughout the addition period and held at 80°C to 85°C for a further 1 hour to ensure complete reaction. After which time the temperature of the reactants was increased to 90°C and held at 90°C for a further 3 hours. This treatment served:—

(a) to decompose excess A.Z.B.N.

(b) to distil out the t-butyl alcohol, which was continuously replaced with light spindle oil during the distillation period. I.e. 300 parts by weight of oil was added to reduce the copolymer concentration to 25% W/W activity. Residual t-butyl alcohol was determined as 2% to 3% W/W on the final material.

(b) Inverse emulsion polymerisation of acrylic acid

The apparatus and procedure was essentially the same as that outlined in Example I, but based on the following composition:

vessel charge	
91.5 parts spindle oil	
8 " 25 W/W stabilizer prepared as in (a) above	
4 " sorbitan mono stearate or mono oleate	
2000 ppm of A.Z.B.N. based on monomer phase.	

The vessel charge was purged as outlined earlier and the monomer phase, 100 parts by weight of 60% W/W acrylic acid solution added over a 2 to 3 hour reaction time, at a vessel temperature of 70°C to 75°C. The reactants were then heated a further 1 hour at 80°C to ensure complete reaction.

A 1% solution of polymer prepared by inverting the emulsion in H₂O yielded a viscosity of 2000 cps, measured by a Brookfield Viscometer.

EXAMPLE IV

Inverse emulsion polymerisation of methacrylic acid

As in Example III but substitute 100 parts of methacrylic acid 60% W/W for 100 parts of acrylic acid.

EXAMPLE V

Inverse emulsion polymerisation of acrylamide

As in Example III but substitute 100 parts of a 60% W/W acrylamide solution for 100 parts of acrylic acid.

EXAMPLE VI

(a) Preparation of stabilizer in perchloroethylene

This was carried out exactly as in Example

I(a) except that the light spindle oil was replaced by perchloroethylene as solvent. The 72.1 parts of solvent (added later in Example I(a)) was included in the first charge to the vessel making a total of 140.8 g. of perchloroethylene. The stabilizer solution was diluted to 25% W/W concentration as before.

(b) Inverse emulsion polymerisation of methyl chloride quaternised dimethylaminoethylmethacrylate

This was performed as in Example I(b) except that 117 parts of perchloroethylene were used in place of light spindle oil, and the stabiliser was that prepared in Example (a) above, in perchloroethylene.

WHAT WE CLAIM IS:—

1. A process for the preparation of a stable dispersion of polymer by emulsion polymerisation which comprises continuously introducing an aqueous solution of monomer to a system containing oil, water-in-oil emulsifier, an emulsion stabilizer which is an oil-soluble copolymer prepared from at least one hydrophobic monomer and at least one hydrophilic monomer, and polymerisation initiator, the system being at the temperature required for polymerisation whereby to effect the polymerisation throughout the continuous addition of monomer.

2. A process as claimed in claim 1 wherein said polymer is derived from water-soluble vinyl monomer.

3. A process as claimed in claim 1 or 2 wherein said oil is a liquid hydrocarbon.

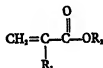
4. A process as claimed in any of the preceding claims for the preparation of dispersions in which the proportion of disperse phase to total emulsion ranges between 25% and 70%.

5. A process as claimed in any one of the preceding claims for the preparation of dispersions of aqueous polymer solutions in which the disperse phase to total emulsion ranges between 25% and 75% and the monomer concentration in the aqueous phase used can be between 20% and 90% on weight of aqueous solution.

6. A process as claimed in any one of the preceding claims wherein said emulsifier is an inverse emulsifying agent in the range 0.1–10 parts per 100 parts by weight of disperse phase.

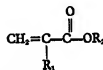
7. A process as claimed in any one of the preceding claims wherein said stabilizer is a polymeric stabilizer in the range 0.1–10 parts per 100 parts of monomer solution.

8. A process as claimed in claim 7 wherein said polymeric stabilizer is a copolymer derived from a hydrophobic monomer (A)



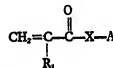
where R_1 is H or CH_3 and R_2 can be C_6 – C_{22} hydrocarbon chain either branched or linear and a hydrophilic monomer (B) which may be anionic

anionic



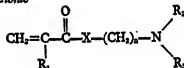
$\text{R}_1=\text{H}$ or CH_3
 $\text{R}_2=\text{H}$

nonionic



$\text{R}_1=\text{H}$ or CH_3
 $\text{X}=\text{NH}$ or O
 $\text{A}=(\text{CH}_2-\text{CH}_2\text{O})_n-\text{H}$ where
 $n=1$ to 20

or cationic



$\text{R}_1=\text{H}$ or CH_3
 $\text{R}_2=\text{C}_6$ – C_{22} hydrocarbon
 $\text{R}_3=\text{C}_6$ – C_{22} hydrocarbon
 R_2 and R_3 can be different
 $\text{X}=\text{O}$ or NH
 $n=1$ – 3

and the molar ratio of type A:B monomers in the copolymer lies in the range 1:3 to 3:1.

9. A process as claimed in claim 8 wherein the molar ratio of type A:B monomers in the copolymer is 1:2 to 2:1.

10. Polymer dispersion whenever produced by a process as claimed in any one of the preceding claims.

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